Claims

1. A fluorine-modified one- or two-component polyurethane resin having improved surface properties, obtainable by

a) preparing a fluorine-modified polyurethane prepolymer having free isocyanate groups or free amino and/or hydroxyl groups, or a fluorine-modified polyol mixture having free hydroxyl groups (binder), where

a_1) a fluorine-modified macromonomer (A1) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 2000 daltons, a higher molecular mass polyol component (A2) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 6000 daltons, and a low molecular mass polyol component (A3)(i) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons

either

is reacted with a polyisocyanate component (B)(i), consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst,

or

if desired, is blended in the presence of a solvent component (L)(i) and in the presence if desired of a catalyst,

a_2) the fluorine-modified polyurethane prepolymer or

polyol mixture from stage a_1) is reacted if desired with an unmodified or fluorine-modified functionalizing component (C)(i) having one or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and/or one or more isocyanate groups that are reactive toward hydroxyl groups and having a molecular mass of 50 to 2500 daltons, selected from the groups of the (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols and/or reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_n$ with n = 4, 6, 8, 10, 12 and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms and a molar mass of 250 to 25 000 daltons,

a_3) the fluorine-modified polyurethane prepolymer or polyol mixture from stages a_1) or a_2) is admixed with a formulating component (F)(i),

and finally

b) by preparing a fluorine-modified polyurethane resin having a polymer-bonded fluorine content of 1% to 4% by weight in the system as a whole by reacting the fluorine-modified polyurethane prepolymer from stage a_3) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a_3) (<u>binder</u>) in the case of a two-component application with a crosslinker component (D) (<u>curing agent</u>), with a formulating component (F)(ii) in the presence if desired of a solvent component (L)(iii) and also of a catalyst, using as crosslinker component (D) in the case of the polyol mixture from stage a_3) a polyisocyanate

component (B)(iii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons and/or a low molecular mass polyamine component (E) having two or more (cyclo)aliphatic or aromatic amino groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons.

2. The fluorine-modified polyurethane resin of claim 1, characterized in that the fluorine-modified macromonomer (A1) has been prepared by

c_1) reacting a fluoro alcohol component (A4) consisting of a perfluoroalkyl alcohol having terminal methylene groups (hydrocarbon spacers), of the general formula

$$CF_3-(CF_2)_x-(CH_2)_y-OH$$
with x = 3 - 20 and y = 1 - 6

or of a hexafluoropropene oxide (HFPO) oligomer alcohol of the general formula

$$CF_3CF_2CF_2O-CF(CF_3)CF_2O)_z-CF(CF_3)CH_2-OH$$
with z = 1 - 10

or else mixtures of these having a hydroxyl group that is reactive toward isocyanate groups and having a molecular mass of 250 to 5000 daltons, with a polyisocyanate component (B)(ii) consisting of at least one diisocyanate, polyisocyanate,

polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, in the presence if desired of a solvent component (L)(ii) and in the presence if desired of a catalyst,

c_2) if desired, reacting the preadduct from stage c_1) completely with a functionalizing component (C)(ii) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons, selected from the group of (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols.

3. The fluorine-modified polyurethane resin of claim 1 or 2, characterized in that as fluorine-modified macromonomer (A1) use is made of reaction products and/or macromonomers, with a monomodal molar mass distribution, of monofunctional perfluoroalkyl alcohols, isophorone diisocyanate or toluene diisocyanate, and diethanolamine.

4. The fluorine-modified polyurethane resin of claim 1, characterized in that as fluorine-modified macromonomer (A1) use is made of optionally solvent-containing reaction products of

i) perfluoroalkylalkenes and diethanolamine, preferably perfluoroalkylalkenes having terminal methylene groups (hydrocarbon spacers), of the general formula

$$CF_3-(CF_2)_x-CH=CH_2$$
with x = 3 - 20

and/or

ii) alkyl (per)fluoro(meth)acrylates and/or (per)fluoroalkyl (meth)acrylates and/or (per)fluoroalkyl (per)fluoro(meth)acrylates and diethanolamine

and/or

iii) (per)fluoroalkylalkylene oxides and N-methylethanolamine or diethanolamine with preferred (per)fluoroalkylalkylene oxides of the general formula

$$CF_3-(CF_2)_x-CH_2-C_2H_3O$$
with x = 3 - 20.

5. The fluorine-modified polyurethane resin of any one of claims 1 to 4, characterized in that use is made as higher molecular mass polyol component (A2) of (hydrophobically modified) polyalkylene glycols, aliphatic or aromatic polyesters, polycaprolactones, polycarbonates, hydroxy-functional macromonomers and telecheles such as α,ω-polymethacrylatediols, α,ω-dihydroxyalkylpolydimethylsiloxanes, hydroxy-functional epoxy resins, hydroxy-functional ketone resins, hydroxy-functional polysulfides, hydroxy-functional triglycerides, oxidatively drying alkyd resins based on bisepoxides and unsaturated fatty acids, or mixtures thereof.

6. The fluorine-modified polyurethane resin of any one of claims 1 to 4, characterized in that use is made as component (A2) of linear and/or difunctional (hydrophobically modified) polyether- and/or polyester- and/or polycaprolactone- and/or polycarbonate-polyols and/or α,ω-polymethacrylatediols having a molecular mass of 500 to 3000 daltons.

7. The fluorine-modified polyurethane resin of any one of claims 1 to 6, characterized in that use is made

as component (A3)(i) and (A3)(ii) of 1,4-butanediol and/or 2-methyl-1,3-propanediol and/or 2,2-dimethyl-1,3-propanediol.

8. The fluorine-modified polyurethane resin of any one of claims 1 to 7, characterized in that use is made as components (B)(i) and/or (B)(ii) and/or (B)(iii) of difunctional polyisocyanate derivatives and/or reaction products of at least trifunctional aliphatic or aromatic polyisocyanates and optionally fluorine-modified amino-functional polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_n$ with n = 4, 6, 8, 10, 12 and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms.

9. The fluorine-modified polyurethane resin of any one of claims 1 to 8, characterized in that component (C)(i) comprises reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_8$ with R = aminopropyl and/or isocyanatopropyl and optionally $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$ and/or H and/or C_1-C_{25}-alkyl and/or C_3-C_{25}-cycloalkyl and/or C_6-C_{30}-aryl and/or $(CH_2)_3(OCH_2CH_2)_nOMe$ and/or epoxypropyl and/or dimethoxysilyloxy and/or methacryloyloxypropyl and/or triethoxysilylpropyl.

10. The fluorine-modified polyurethane resin of any one of claims 1 to 9, characterized in that use is made as component (C)(i) of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula

$$(R_aX_bSiO_{1.5})_m$$

with a = 0 or 1
b = 0 or 1
a+b = 1
m = 4, 6, 8, 10, 12,

and

R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, which in each case is substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, which are attached via a polymer unit or a bridging unit,

X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type R that contain at least one such group of type X,

the substituents of type R and the substituents of type X each being identical or different.

11. The fluorine-modified polyurethane resin of any one of claims 1 to 10, characterized in that (cyclo)aliphatic and/or aromatic polyamines and/or amino alcohols are used as low molecular mass polyamine component (E).

12. The fluorine-modified polyurethane resin of any one of claims 1 to 11, characterized in that latent curing agents based on aldimines and/or ketimines and/or enamines are used as low molecular mass polyamine component (E).

13. The fluorine-modified polyurethane resin of any one of claims 1 to 12, characterized in that as formulating component (F)(i) and (F)(ii) use is made of defoamers, devolatilizers, lubricity and flow-control additives, dispersing additives, substrate wetting

additives, water repellents, rheology additives, coalescence assistants, matting agents, adhesion promoters, antifreeze agents, antioxidants, UV stabilizers, bactericides, fungicides, further polymers, and also fillers, pigments, nanoparticles or a suitable combination thereof.

14. The fluorine-modified polyurethane resin of any one of claims 1 to 13, characterized in that the NCO/OH equivalent ratio of components (A1), (A2), (A3)(i), and (B)(i) in stage a) is set at a level of 0.5 to 10.0, preferably 1.5 to 6.0.

15. The fluorine-modified polyurethane resin of any one of claims 1 to 14, characterized in that the NCO/OH equivalent ratio of components (A4) and (B)(ii) in stage c_1) is set at 1.9 to 2.1 and the NCO/OH+NH equivalent ratio of the components in the preadduct from stage c_1) and (C)(ii) in stage c_2) is set at 0.95 to 1.05.

16. The fluorine-modified polyurethane resin of any one of claims 1 to 15, characterized in that the NCO/OH equivalent ratio of binder and curing agent in stage b) is set at a level of 1.0 to 2.0, preferably 1.0 to 1.5.

17. The fluorine-modified polyurethane resin of any one of claims 1 to 16, characterized in that reaction stages a), b), and c) are carried out in the presence of 0.01% to 1% by weight, based on components (A) and (B), of a catalyst which is customary for polyaddition reactions with polyisocyanates.

18. The fluorine-modified polyurethane resin of any one of claims 1 to 17, characterized in that in stage a) the solids content of fluorine-modified polyurethane prepolymer or polyol mixture, consisting of components (A1), (A2), (A3)(i), (B)(i), and (C)(i), is set at 25% to 100% by weight, preferably 50% to 75% by weight,

based on the total amount of the binder, consisting of components (A1), (A2), (A3)(i), (B)(i), optionally (C)(i), (F)(i), optionally (L)(i) and optionally (L)(iii).

19. The fluorine-modified polyurethane resin of any one of claims 1 to 18, characterized in that in stage b) the solids content of crosslinker component, consisting of components (B)(iii) and (B)(iii) or (A3)(ii) and/or (E), respectively, is set at 25% to 100% by weight, preferably 50% to 75% by weight, based on the total amount of curing agent (D), consisting of components (B)(iii) or (A3)(ii) and/or (E), (F)(ii) and, if desired, (L)(iii).

20. The fluorine-modified polyurethane resin of any one of claims 1 to 19, characterized in that the polyurethane polymer, consisting of components (A), (B), (C), and (E), has an average molecular mass (number average) of 10 000 to 100 000 daltons.

21. A process for preparing the fluorine-modified polyurethane resin of claims 1 to 20, characterized in that

a) a fluorine-modified polyurethane prepolymer or polyol mixture (binder) is prepared by

a_1) reacting components (A1), (A2), and (A3)(i) either with component (B)(i) in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst, some or all of the hydroxyl groups of components (A1), (A2), and (A3)(i) being reacted with the isocyanate groups of component (B)(i), or blending said components in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst,

a_2) if desired, reacting the fluorine-modified polyurethane prepolymer or the polyol mixture from stage a_1) with an optionally fluorine-modified functionalizing component (C)(i),

a_3) admixing the fluorine-modified polyurethane prepolymer or polyol mixture from stages a_1) or a_2) with a formulating component (F)(i), the formulating constituents being added individually or together before, during or after the reaction or blending of the individual components, and

b) a fluorine-modified polyurethane resin is prepared by reacting the fluorine-modified polyurethane prepolymer from stage a_3) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a_3) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), a formulating component (F)(ii), and, if desired, a solvent component (L)(iii), in the presence if desired of a catalyst, using as crosslinker component (D) in the case of the polyol mixture a polyisocyanate component (B)(iii) and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) and/or a low molecular mass polyamine component (E), and adding the formulating constituents individually or together before, during or after the blending of the individual components.

22. The process of claim 21, characterized in that the fluorine-modified macromonomer (A1) is prepared by

c_1) reacting a fluoro alcohol component (A4) with the polyisocyanate component (B)(ii) in the presence if desired of a solvent component (L)(ii) and in

the presence if desired of a catalyst, the reaction conditions and the selectivities of components (A4) and (B)(ii) being chosen such that only one isocyanate group of component (B)(ii) reacts with component (A4), and subsequently

c_2) if desired, reacting the preadduct from stage c_1) completely with the functionalizing component (C)(ii), the reaction conditions and the selectivity of component (C)(ii) being chosen such that only one reactive group of component (C)(ii) reacts with the free isocyanate group(s) of the preadduct.

23. The process of any one of claims 20 to 22, characterized in that reaction stages a_1) and a_2) are carried out at a temperature of from 40 to 120°C, preferably at 50 to 110°C.

24. The process of any one of claims 20 to 23, characterized in that reaction stages a_3) and b) are carried out at a temperature of from 10 to 60°C, preferably at 20 to 50°C.

25. The process of any one of claims 20 to 24, characterized in that reaction stages c_1) and c_2) are carried out at a temperature of from -20 to 50°C, preferably at 0 to 30°C.

26. The use of the fluorine-modified polyurethane resins of claims 1 to 20 in the construction or industrial sector for the permanent oil- and water-repellent surface treatment or modification of mineral and nonmineral substrates, such as

- Inorganic surfaces,
  such as porous, absorbent, rough, and polished construction materials and building materials of all kinds (such as concrete, gypsum, silica and

silicates, artificial stone, and natural stone (such as granite, marble, sandstone, slate, and serpentine), clay, cement, brick) and also enamels, fillers and pigments, glass, ceramic, metals and metal alloys,

- Organic surfaces,
  such as wood and woodbase materials, wood veneer, glass fiber-reinforced plastics (GRP), plastics, leather, natural fibers, polar organic polymers of all kinds, and composite materials.

27. The use of the fluorine-modified polyurethane resins of claims 1 to 20 for the permanent oil- and water-repellent surface treatment or modification in the construction sector
such as
- antigraffiti/antisoiling coatings
- easy to clean coatings
- further coatings of all kinds (such as balcony coatings, roof(tile) coatings, baking varnishes, paints and varnishes, masonry paints, floor coatings, light-, medium- and heavy-duty industrial floors, carpark surfacings, sports floors)
- seals
- prefabricated concrete components
- concrete moldings
- tiles and joints
- adhesives and sealants
- soundproofing walls
- corrosion control
- renders and decorative plasters
- external insulation and finishing systems (EIFS) and external insulation systems (EIS)

28. The use of the fluorine-modified polyurethane resins of claims 1 to 19 in the sector of
- automobile industry
- coil coatings

- baking varnishes
- glass facades and glass surfaces
- ceramics, including sanitary ceramics
- leather dressing
- surface-modified fillers and pigments
- paper coating
- rotors of wind turbines
- marine paints.

29. The use of the fluorine-modified polyurethane resins of claims 1 to 19 in the construction or industrial sector for the integral water/oil repellency treatment of concrete, such as

- prefabricated concrete components
- concrete moldings
- cast-in-place concrete
- shotcrete
- ready-mix concrete.